

An inland sea high nitrate-low chlorophyll (HNLC) region with naturally high pCO₂

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Abstract

We present a time series of data for temperature, salinity, nitrate, and carbonate chemistry from September 2011 to July 2013 at the University of Washington's Friday Harbor Laboratories. Samples were collected at the Friday Harbor dock and pump house. Seawater conditions at Friday Harbor were high nitrate-low chlorophyll, with average nitrate and pCO₂ concentrations of $\sim 25 \pm 5 \mu\text{mol L}^{-1}$ and $\sim 700 \pm 103 \mu\text{atm}$ (pH 7.80 ± 0.06). Transient decreases in surface water nitrate and pCO₂ corresponded with the timing of a spring bloom (April through June). The high nitrate and pCO₂ originate from the high values for these parameters in the source waters to the Salish Sea from the California Undercurrent (CU). These properties are due to natural aerobic respiration in the region where the CU originates, which is the oxygen minimum zone in the eastern tropical North Pacific. Alkalinity varies little so the increase in pCO₂ is due to inputs of dissolved inorganic carbon (DIC). This increase in DIC can come from both natural aerobic respiration within the ocean and input of anthropogenic CO₂ from the atmosphere when the water was last at the sea surface. We calculated that the anthropogenic "ocean acidification" contribution to DIC in the source waters of the CU was $36 \mu\text{mol L}^{-1}$. This contribution ranged from 13% to 22% of the total increase in DIC, depending on which stoichiometry was used for C/O₂ ratio (Redfield vs. Hedges). The remaining increase in DIC was due to natural aerobic respiration.

The surface ocean is growing more acidic due to uptake of anthropogenic CO₂ (Brewer 2000; Caldeira and Wickett 2003). As a result, marine ecosystems, the services they provide for humanity, and the societies they support are at risk. Impacts of ocean acidification (OA) will be felt across all ocean basins but are intensified in many coastal areas due to natural processes like upwelling, freshwater input and local respiration (Duarte et al. 2013). Over time, as atmospheric CO₂ continues to increase, the biological consequences of OA can propagate through marine food webs, from the lowest to the highest levels, including species valued as food resources for humans (Fabry et al. 2008; Hall-Spencer et al. 2008; Portner 2008).

In urbanized coastal regions and estuaries there are three sources for acidification of the ocean. One is natural and two are anthropogenic. In all three cases the increases in pCO₂ are due to increases in dissolved inorganic carbon (DIC) rather than decreases in alkalinity. The increase in DIC is calculated from the increasing pCO₂ at constant alkalinity.

1. Classic "ocean acidification" is due to the increase in DIC resulting from equilibration of surface seawater with increasing CO₂ in the atmosphere (where it is steadily increasing) (e.g., Feely et al. 2004; Sabine et al. 2004). The well-documented data from the Hawaiian Ocean Time Series (HOT) (e.g., Doney et al. 2009; Dore et al. 2009) and the Bermuda Atlantic Time Series (BATS) (e.g., Bates et al. 2012) are good examples.
2. Natural acidification of the ocean is due to aerobic respiration of organic carbon, which results in elevated CO₂, lower pH, lower oxygen, and higher nutrient concentrations. Examples include ocean oxygen minimum zones,

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coastal upwelling regions with high biological production and locations where mixing is limited by geography (e.g., inlets, estuaries, and bays) (e.g., Feely et al. 2008; Barton et al. 2012).

3. Anthropogenic acidification due to eutrophication where nutrients of anthropogenic origin enhance organic matter production, which is then respired to produce CO_2 . A possible example is the southern part of Hood Canal located in Puget Sound, Washington where there is concern that nutrients from terrestrial runoff may stimulate additional production of organic matter that is respired to CO_2 (Feely et al. 2010). Another example is Chesapeake Bay where the sedimentary record shows a marked increase in anthropogenic influence (Zimmerman and Canuel 2000).

It is often difficult to distinguish anthropogenic “ocean acidification” from acidification due to natural respiration, especially in coastal environments. The forcing functions for each CO_2 source vary on different temporal and spatial scales and observations intending to evaluate their importance need to vary accordingly.

The data described here were obtained at the University of Washington’s Friday Harbor Laboratories (FHL) on San Juan Island, Washington, U.S.A. San Juan Island is in the Salish Sea at the northeastern end of the Juan de Fuca Strait and between Puget Sound and the Strait of Georgia. In this article, we describe the new Ocean Acidification Experimental Lab (OAEL) at the University of Washington’s Friday Harbor Marine Laboratories (FHL). We then report the results from a time series of nutrient and carbonate system data for seawater at the dock in Friday Harbor. Estimates for the anthropogenic contribution to OA are made for the California Undercurrent (CU), which is the source of the high levels of $p\text{CO}_2$ surrounding San Juan Islands.

Experimental and analytical facilities

The University of Washington has constructed a state of the art OAEL facility at the FHL that offers unique research and instructional opportunities for experimental manipulations with on-site analyses of carbonate system parameters. FHL’s location, facilities, and educational mission combine to make this an ideal site for the experimental facility. Its location allows experimentation on organisms native to the northeastern Pacific, where acidification and its impacts have already been detected. This facility consists of a new 1500 sq. ft. experimental lab that includes a carbonate system analytical laboratory, indoor microcosms, and in-water mesocosms (<http://depts.washington.edu/fhl/oael.html>).

The carbonate system analytical lab provides carbonate system analyses (DIC, alkalinity, pH, P_{CO_2}) in support of all experiments. pH is measured using the spectrophotometric technique described in Standard Operating Procedure (SOP) 6b (Clayton and Byrne 1993; Dickson et al. 2007) using an Ocean Optics CCD spectrophotometer with temperature-controlled 10 cm

path length cells. A custom-built, IR-based analyzer is used for total DIC analyses of water samples (Friederich et al. 2002). Total alkalinity (TA) is measured by acidimetric titration using an open cell titrator as outlined in SOP 3b (Dickson et al. 2007). Standards for DIC are prepared as a series of sodium carbonate solutions (SOP 14) (Dickson et al. 2007). Certified Reference Materials are analyzed with both DIC and TA samples as an independent verification of calibrations (Dickson et al. 2007). At present the precision and accuracy of both the DIC and TA analyses are about $\sim 1\text{--}4\ \mu\text{mol L}^{-1}$ and $\sim 1.5\ \mu\text{eq L}^{-1}$, respectively, based on our participation in two recent National Oceanic and Atmospheric Administration OA lab intercalibrations organized by Dr. Andrew Dickson (SIO, UCSD).

Methods

Time series

A time series of samples was collected at the FHL dock for nutrients and carbonate system parameters prior to, during and after, mesocosm experiments that were conducted in April 2012 and 2013. Samples were collected mid-day from a depth of three meters at the end of the FHL dock using a 2.5 L Niskin bottle. Samples were obtained once a week from July 2011 to August 2013. Temperature and salinity were measured using a SeaBird Internally Recording CTD Model SBE 37-SMP. During the April 2012 and April 2013 mesocosm experiments samples were collected daily. Additional samples were collected weekly from July 2011 to July 2013 from a seawater stream originating from Cantilever Point (two meters below mean low low water; mid-day) at the FHL pump house. Pump house temperature and salinity were recorded continuously with a deployed CT (SeaBird Microcat; live data at <http://depts.washington.edu/fhl/wx.html>).

Analytical

Oxygen was analyzed using the standard Winkler Method (Carpenter 1965). Salinity in the Cantilever Point pump-house stream was monitored using a Honeywell conductivity sensor. Samples for nitrate were prefiltered and analyzed on a Technicon Autoanalyzer II. Nitrate was reduced to nitrite using a cadmium column, then nitrite was measured using sulphanilamide and *N*(1-naphthyl)-ethylenediamine (Armstrong et al. 1967). Samples for chlorophyll were filtered onto GFF filters and analyzed by fluorometry (Parsons et al. 1984) with a Turner TD-700 Fluorometer. DIC and alkalinity were analyzed as described above in the section on Facilities.

Results

This was the first time series of data for temperature, salinity, oxygen, nutrients, chlorophyll, and carbonate system parameters at the FHL. These data provided the temporal context for OA mesocosm experiments conducted in April 2012 and April 2013 (Murray et al., unpubl).

The record of salinity and temperature in FHL pump house samples from July 2011 to July 2013 is shown in

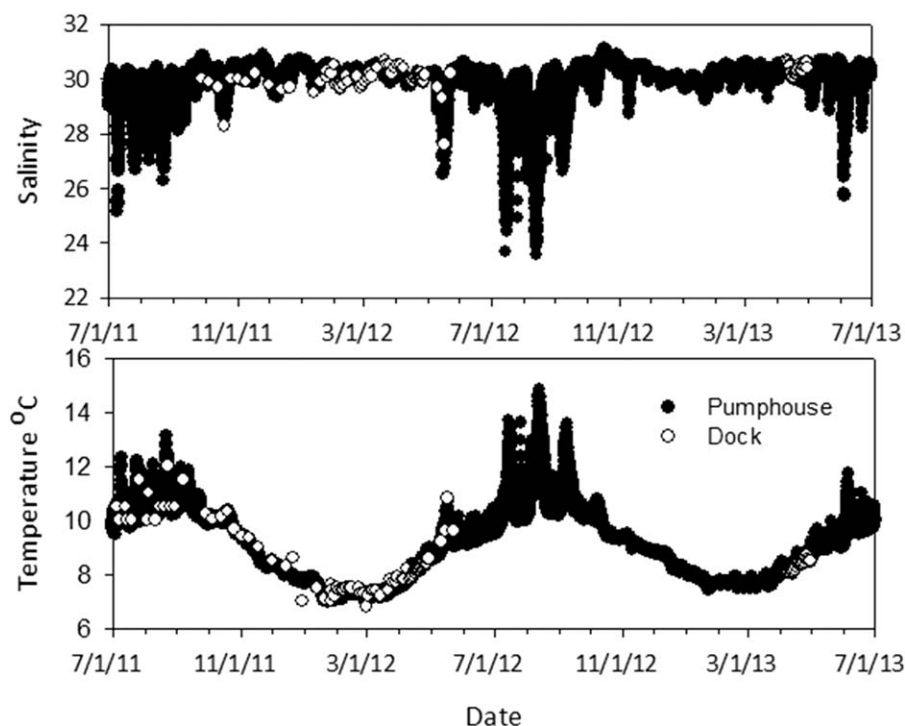


Fig. 1. Time record from July 2011 to August 2013 of salinity and temperature at the FHL Dock (open symbols), measured using a SeaBird CTD (Model SBE37-SMP) and in pump house samples (dark symbols) measured using a SeaBird Microcat, mounted at 1.7 m depth.

Fig. 1. The salinity was normally about $S = 30$ but fluctuated from values lower than 24 to almost 31. These values of surface salinity reflect the variability in the relative influence of freshwater input from the Fraser River, Canada vs. inflow of seawater from the Strait of Juan de Fuca. Voss et al. (2014) recently conducted extensive analyses of dissolved inorganic constituents of the Frazer River and reported that the discharge-weighted average concentration of HCO_3^- in the Fraser River was $851 \pm 74 \mu\text{mol L}^{-1}$. As the DIC and alkalinity of the Fraser River are low (and approximately equal) this would result in negative anomalies when lower salinity is present. That may explain some of the lower values of DIC and alkalinity seen at FHL in July 2012 and 2013 (Fig. 2). The temperature reflected both seasonal climate forcing and variability in source water. The values were about 11°C in July 2011 and August 2012 and decreased to less than 8°C in the winter in March 2012 and March 2013. During spring and summer periods of higher freshwater input from the Fraser River the temperature spiked to higher values, perhaps due to stronger stratification.

The concentrations of nitrate, nitrite, ammonia, phosphate, and silicate were analyzed from July 2011 to May 2012 and in April 2013 and the nitrate data are shown in Fig. 2. These may be the first nutrient analyses ever conducted at the FHL dock. Nitrate concentrations ranged from $\sim 17 \mu\text{mol L}^{-1}$ to $\sim 30 \mu\text{mol L}^{-1}$ but were almost always greater than $20 \mu\text{mol L}^{-1}$. Nitrate decreased after early March 2012 from $28 \mu\text{mol L}^{-1}$ to $18 \mu\text{mol L}^{-1}$ in May 2012. It was not possible to analyze nutrients between May 2012 and April 2013 because of fund-

ing and logistical issues, but we can posit that nutrients remained high during that period because of the high values of DIC and $p\text{CO}_2$. Nitrite (not shown) was always less than $0.3 \mu\text{mol L}^{-1}$, but there were some trends to the data. The lowest values ($\sim 0.10 \mu\text{mol L}^{-1}$) were from November to March when nitrate was at its highest values. Ammonium (not shown) was about $2 \mu\text{mol L}^{-1}$ from August 2011 to March 2012 when it decreased abruptly to less than $1 \mu\text{mol L}^{-1}$. It increased steadily back to $2 \mu\text{mol L}^{-1}$ in April 2012. Phosphate (not shown) was slightly greater than $2.0 \mu\text{mol L}^{-1}$ for most of the time series and, like nitrate, decreased after March 2012. The decrease in nitrate and phosphate from March to May 2012 corresponded to an N/P removal ratio of 13.3, slightly more P rich biological uptake than the Redfield Ratio of 16. Silicate (not shown) was about $55 \mu\text{mol L}^{-1}$ for most of the time series and decreased from March to May 2012 to $33 \mu\text{mol L}^{-1}$. The variability of both phosphate and silicate were similar to that for nitrate and the concentration of all three both decreased from March to May.

The record of carbonate system data covered September 2011 to August 2013. DIC and alkalinity were measured. $p\text{CO}_2$ and pH were calculated using the computer program CO_2Calc (Robbins et al. 2010) for the measured salinity and temperature. In September 2011, the values for DIC, Alk, $p\text{CO}_2$, and pH were $2033 \pm 28 \mu\text{mol L}^{-1}$, $2087 \pm 21 \mu\text{mol L}^{-1}$, $785 \pm 106 \mu\text{atm}$ and 7.76 ± 0.05 , respectively ($n = 13$ –20, pooled dock and pump house site). In April 2012, the values were $1994 \pm 17 \mu\text{mol L}^{-1}$, $2081 \pm 6 \mu\text{mol L}^{-1}$, $557 \pm 100 \mu\text{atm}$ and 7.89 ± 0.07 ($n = 20$ –22). The DIC decreased

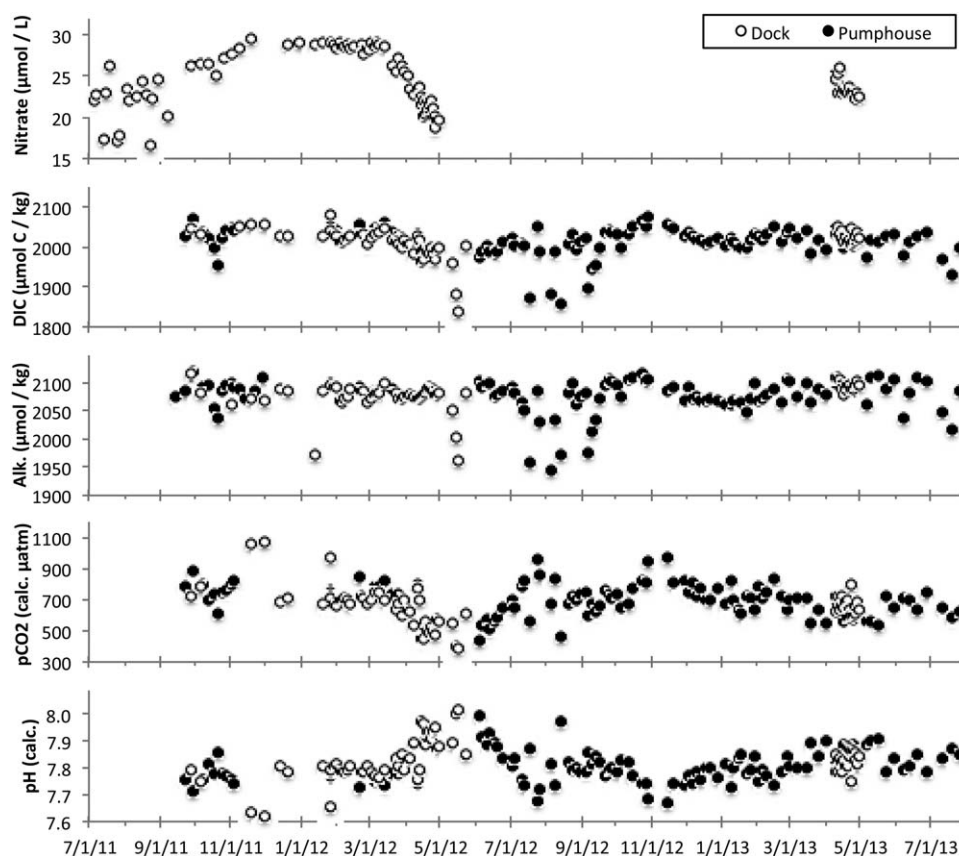


Fig. 2. Time record of nitrate, DIC, alkalinity, $p\text{CO}_2$ (calculated from DIC and alkalinity) and pH (calculated from DIC and alkalinity) at the Friday Harbor Lab dock from July 2011 to August 2013.

slowly while the alkalinity stayed constant. No attempt was made to identify the noncarbonate fraction of the alkalinity (e.g., Kim and Lee 2009). Our analyses of DOC were in the uniformly in the range of $80\text{--}110\ \mu\text{mol C L}^{-1}$; slightly higher than average open ocean surface seawater but not enough to impact these results. The $p\text{CO}_2$ was consistently greater than $650\ \mu\text{atm}$ (Fig. 2). The $p\text{CO}_2$ decreased to $\sim 400\ \mu\text{atm}$ for a short period in May 2012, most likely due to biological production, but then rapidly returned to values greater than $650\ \mu\text{atm}$ by July 2012 (avg, $p\text{CO}_2 = 683 \pm 115$, $n = 176$). The drawdown of $p\text{CO}_2$ in 2013 was less evident. pH was constant at about 7.80 (avg pH = 7.82 ± 0.07 , $n = 176$) except for a brief increase in May 2012 when $p\text{CO}_2$ was drawn down.

Chlorophyll and oxygen are also tracers for biologically produced organic matter. Chlorophyll at the dock was always less than or equal to $\sim 1\ \mu\text{g L}^{-1}$ with no systematic variability (not shown). Taken together, the nitrate and chlorophyll data show that seawater in Friday Harbor is high nitrate low chlorophyll (HNLC). Oxygen at the dock (not shown) was fairly constant at about $270\ \mu\text{mol L}^{-1}$. This concentration is about 80% atmospheric saturation for the in situ temperature and salinity.

Discussion

High nitrate, high CO_2 , low chlorophyll conditions at FHL

For most of the year the seawater at the Friday Harbor Labs dock had concentrations of NO_3^- ranging from $\sim 17\ \mu\text{mol L}^{-1}$ to $\sim 30\ \mu\text{mol L}^{-1}$, chlorophyll = $1\ \mu\text{g L}^{-1}$ and $p\text{CO}_2 = 650\ \mu\text{atm}$. High nitrate, low chlorophyll, and high CO_2 conditions exist in seawater around San Juan Island. The year round seawater conditions at the FHL pump house site had a $p\text{CO}_2$ of $700 \pm 103\ \mu\text{atm}$ and pH 7.80 ± 0.06 . Surface seawater away from shore northeast and southeast of the San Juan Islands appears to have similar conditions (Autumn 2011 $p\text{CO}_2$ ranging 711–1081; pH 7.67–7.80) (Sullivan 2013). In fact, the surface seawaters of most of Puget Sound have $p\text{CO}_2$ concentrations greater than the atmospheric so the CO_2 flux is from Puget Sound to the atmosphere (Feely et al. 2010). These variable but high $p\text{CO}_2$ levels suggest two things:

1. The surface seawater around the San Juan Islands has HNLC conditions. The classic explanation for HNLC conditions is iron limitation (Martin et al. 1994). No data for iron concentrations are available for this location, but it is

very unlikely that HNLC conditions exist at FHL because of iron limitation. Dissolved iron is sufficiently high for biological demand in the coastal waters of Washington (Bruland et al. 2008) and Oregon (Chase et al. 2002) and the San Juan Islands consist largely of ocean basalt, thus it is unlikely that iron limitation exists there.

2. The coasts of these islands are bathed in seawater with $p\text{CO}_2$ concentrations not expected in the open ocean until the end of this century (IPCC 2013). This means that the UW Friday Harbor Labs and the San Juan Islands, where scientists from around the world come to study the vibrant biological community, are bathed in an OA world of the future. Other locations with such high $p\text{CO}_2$ exist. These include coastal waters of the US West Coast where concentrations of $p\text{CO}_2$ in surface waters can reach 800–1100 μatm (e.g., van Geen et al. 2000; Feely et al. 2008), Kiel Fjord, where $p\text{CO}_2$ reaches 1700–3200 μatm (e.g., Melzner et al. 2013), $p\text{CO}_2$ rich water from shallow volcanic vents such as the sites off Ischia, Italy (e.g., Hall-Spencer et al. 2008) where $p\text{CO}_2$ concentrations can exceed 2000 μatm and around islands near Papua New Guinea (e.g., BIOACID project; www.bioacid.de/?idart=830&idlang=32). These high $p\text{CO}_2$ sites are spatially variable and provide excellent opportunities to study biological adaptation to high $p\text{CO}_2$ levels.

Coastal seawater origin: California Undercurrent as a CO_2 source

The high nitrate and $p\text{CO}_2$ conditions around the San Juan Islands exist because the seawater end-member originates during upwelling from the CU on the Washington Coast. Northerly, upwelling favorable, winds predominate in the summer (e.g., Hickey 1998). The CU is a seasonal poleward flow present over the upper continental slope of the west coast of North America (Hickey 1979, 1989). The depth of the core density ($\sigma_t = 26.5 \text{ kg m}^{-3}$) shoals toward the north and off the coast of Washington it is located between 125 m to 325 m (Pierce et al. 2012). Its nominal properties there are $T = 8.0^\circ\text{C}$, $S = 33.8$ and dissolved oxygen = 89 μM (about 30% of atmospheric saturation).

Some of the variability in the nature of the upwelled water depends on variability in the depth of the upwelling cell which varies with the Pacific Decadal Oscillation (PDO) (Meinvielle and Johnson 2013). Changes in the large-scale winds are primarily responsible. The upwelling cell extends deeper during the negative or “cool” phase of the PDO than during the positive or “warm” phase (Chhak and Di Lorenzo 2007; Meinvielle and Johnson 2013). In 2012, the PDO was in a cool phase, thus more favorable to upwelling waters with lower oxygen and higher nitrate and CO_2 .

The upwelled CU seawater is derived from the mixing of two sources, the warmer, saltier Pacific Equatorial Water (PEW), and colder, fresher Pacific Subarctic Upper Water (PSUW) (Thomson and Krassovski 2010). Warm, salty, low oxygen, high nutrient, and high $p\text{CO}_2$ PEW (this is the 13°C

Water from Tsuchiya 1981, 1989) travels poleward, after traversing the eastern tropical North Pacific oxygen minimum zone (Garfield et al. 1983; Castro et al. 2001; Thomson and Krassovski 2010). The main source of this water is far south in the Southern Hemisphere (core density of $\sigma_t = 26.5 \text{ kg m}^{-3}$ in the eastern equatorial Pacific). Both Toggweiler et al. (1991) and Rodgers et al. (2003) placed the source at $\sim 50^\circ\text{S}$; 150°W , in the west-central South Pacific. Seawater at a density of $\sigma_t = 26.5$ is also the density of the lowest oxygen concentration and the secondary nitrite maximum (due to denitrification) in the ETNP oxygen minimum (Garfield et al. 1983). As the CU flows poleward along North America, it mixes laterally with colder, fresher PSUW (e.g., Collins et al. 2004). The site where the $\sigma_t = 26.5$ isopycnal of the PSUW outcrops is west of the dateline in the northwestern North Pacific (near 50°N , 170°E) (Johnson and McPhaden 1999). Because of this lateral mixing, the contribution of the low O_2 PEW southern end-member decreases poleward and off the Washington coast the CU has nominal contributions of 40% PEW and 60% PSUW (Thomson and Krassovski 2010). Understanding these natural sources is important for understanding the impact of anthropogenic OA as these two end-members follow very different routes (e.g., North vs. South Pacific) and must have significantly different ages since last contact with the atmosphere.

The properties of the CU vary spatially and temporally reflecting variability in the influence of the PEW (Meinvielle and Johnson 2013). For the period from 1980 to 2012, there appeared to be a northward shift in the contribution of low- O_2 PEW end-member off the coast of Oregon and Washington. This may explain the increased occurrence of coastal hypoxia in some areas (Grantham et al. 2004; Chan et al. 2008; Crawford and Peña 2013), although declines in oxygen in the North Pacific may also play a role (Whitney et al. 2007). There is also support for the hypothesis that global warming will intensify upwelling favorable winds in eastern boundary current systems (Bakun 1990; Sydeman et al. 2014). That could also result in a systematic change in the nature of upwelled water from the California Current system.

Local seawater mixing

After the water is upwelled, there is additional consumption of oxygen and production of CO_2 and nitrate due to respiration in shelf sediments (Connolly et al. 2010; Bianucci et al. 2011) and in the shelf water column (Siedlecki et al. 2015). Respiration in the water and sediments contribute about equally to the additional oxygen consumption on the shelf. The details of how this low O_2 , high nitrate and CO_2 upwelled water transects the shelf to become the deep estuarine inflow of the Strait of Juan de Fuca are complex: upwelling water is channelled through a submarine canyon and into the Strait of Juan de Fuca as an estuarine return flow (Connolly and Hickey 2014). This deep inflow is eventually mixed into the surface estuarine outflow to become the

Table 1. Summary of carbonate system calculation to evaluate the relative contributions of changes in atmospheric $p\text{CO}_2$ and aerobic respiration in the ocean to acidification of the ocean. Assume: Steady state, constant alkalinity, and changes in DIC are due to changing inputs of CO_2 from the atmosphere or aerobic respiration. Today in the California Undercurrent $\sigma_t = 26.5$: $T = 8^\circ\text{C}$; $S = 33.8$, $\text{Alk} = 2250 \mu\text{mol L}^{-1}$, $\text{DIC} = 2188 \mu\text{mol L}^{-1}$, water age since last atmospheric contact = 25–50 yrs pre-industrial on $\sigma_t = 26.5$: $\text{DIC} = 2023 \mu\text{mol L}^{-1}$, atmospheric $p\text{CO}_2 = 280 \mu\text{atm}$ 100 yr ago on $\sigma_t = 26.5$: atmospheric $p\text{CO}_2 = 300 \mu\text{atm}$ 50 yr ago on $\sigma_t = 26.5$: atmospheric $p\text{CO}_2 = 318 \mu\text{atm}$ 25 yr ago on $\sigma_t = 26.5$: atmospheric $p\text{CO}_2 = 350 \mu\text{atm}$

	Preindustrial	100 yr ago	50 yr ago	25 yr ago	CU now
$p\text{CO}_2 (\mu\text{atm})$	280	300	318	350	
$\text{DIC} (\mu\text{mol L}^{-1})$	2023	2036	2045	2061	2188
$\Delta\text{DIC} (\mu\text{mol L}^{-1})$		13	22	38	165
$\text{O}_2 (\mu\text{mol L}^{-1})$	275				89
$\Delta\text{O}_2 (\mu\text{mol L}^{-1})$					186
$\Delta\text{NO}_3 \phi\rho\sigma\mu \Delta\text{O}_2$					19.5
$\Delta\Delta\text{IX} \phi\rho\sigma\mu \Delta\text{O}_2$					129

nutrient rich surface water around the San Juan Islands (Mackas et al. 1987; Thomson et al. 2007; MacFadyen et al. 2008; Sutherland et al. 2011; Johannessen et al. 2014).

Anthropogenic component of DIC due to ocean acidification

The potential influence of OA has been previously estimated for the continental shelf (Feely et al. 2008) and Puget Sound (Feely et al. 2010). Because the O_2 concentrations are so low in the CU the natural contribution of DIC from aerobic respiration must be very large but how large is the anthropogenic contribution? We have undertaken an independent estimate of the relative importance of the anthropogenic vs. the natural contribution due to aerobic respiration (Table 1). Representative present day values of alkalinity and DIC in the core of the CU off the Washington coast (on $\sigma_t = 26.5$) are $2250 \mu\text{mol L}^{-1}$ and $2188 \mu\text{mol L}^{-1}$, respectively (Feely et al. 2008). We assume that the alkalinity was the same value when this water was back at the ocean surface (independent of whether the transport route was PEW or PSUW) (Key et al. 2004; Lee et al. 2006). Seawater at the atmospheric outcrop with this alkalinity in equilibrium with preindustrial $p\text{CO}_2$ of $280 \mu\text{atm}$ would have $\text{DIC} = 2023 \mu\text{mol L}^{-1}$. Based on these calculations, the difference between the DIC on the Washington coast and the preindustrial outcrop equals $165 \mu\text{mol L}^{-1}$. This increase is due to the sum of CO_2 from aerobic respiration plus that from anthropogenic “ocean acidification.”

For the contribution from natural aerobic respiration we calculated that the dissolved oxygen in CU seawater with $T = 8^\circ\text{C}$ and $S = 33.8$, in equilibrium with the atmosphere, would be $275 \mu\text{mol L}^{-1}$. Dissolved oxygen (O_2) in the CU on

$\sigma_t = 26.5$ was $89 \mu\text{mol L}^{-1}$ ($\sim 2 \text{ mL L}^{-1}$) (Feely et al. 2008). Assuming Redfield ratios of N/O_2 and C/O_2 , the apparent oxygen utilization would have been $275 - 89 = 186 \mu\text{mol L}^{-1}$, which would have produced $21.6 \mu\text{mol L}^{-1}$ of NO_3^- and $143 \mu\text{mol L}^{-1}$ of DIC. These amounts would be 10% lower ($\Delta\text{NO}_3^- = 19.5 \mu\text{mol L}^{-1}$ and $\Delta\text{DIC} = 129 \mu\text{mol L}^{-1}$) using the stoichiometric ratios of Hedges et al. (2002). We prefer the amounts predicted by the Hedges Ratios as they are based on direct analyses of the organic compounds in marine organic matter. They show that the oxidation state of plankton carbon is more reduced (oxidation state = -II) and lipid like (CH_2) than that in the formulation of the Redfield equation (CH_2O) where the oxidation state = 0. Thus, in the Hedges version more oxygen is required to oxidize organic carbon to CO_2 . That means that the amount of DIC from “ocean acidification” is equal to $165 - 129 = 36 \mu\text{mol L}^{-1}$ or 22%. This contribution would be 13% of the total increase in DIC using the classic Redfield ratios.

It also means that when this seawater was back at the surface it had a “preformed” $\text{DIC} = 2188 - 129 = 2059 \mu\text{mol L}^{-1}$. Seawater with the alkalinity of the CU in equilibrium with preindustrial $p\text{CO}_2$ of $280 \mu\text{atm}$ would have $\text{DIC} = 2023 \mu\text{mol L}^{-1}$. But if the age of the CU seawater since last contact with the atmosphere at Washington coast varied, the initial concentrations of DIC would have varied depending on the atmospheric $p\text{CO}_2$ at that time. The atmospheric $p\text{CO}_2$ that this future CU water would have equilibrated with would have been $\sim 300 \mu\text{atm}$ (age of 100 yr), $\sim 318 \mu\text{atm}$ (age of 50 yr) or $\sim 350 \mu\text{atm}$ (age of 25 yr) as estimated from the Mauna Loa time record for atmospheric CO_2 (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>). The resulting “preformed” DIC would be $2036 \mu\text{mol L}^{-1}$ for 100 yr, $2045 \mu\text{mol L}^{-1}$ for 50 yr and $2061 \mu\text{mol L}^{-1}$ for 25 yr. Because the present day “preformed” DIC is $2059 \mu\text{mol L}^{-1}$ this suggests that the “apparent” age of the seawater in the CU off Washington must be close to 25 yr.

This estimate of the “ocean acidification” contribution to DIC ($36 \mu\text{mol L}^{-1}$) agrees well with that ($31 \pm 4 \mu\text{mol L}^{-1}$) estimated by Feely et al. (2008, 2010), who based their calculations with reference to anthropogenic DIC (ΔC^*) at stations in the Northeast Pacific (Sabine et al. 2002). A contribution of anthropogenic OA to DIC of 13–22% may seem relatively low at present. But although the natural contribution from aerobic respiration is large and variable, the anthropogenic and natural contributions are additive (Barton et al. 2012). The anthropogenic contribution will only increase in the future as seawater equilibrated with higher atmospheric $p\text{CO}_2$ reaches the coast of Washington. Feely et al. (2008) suggested this amount was already enough to decrease the aragonite saturation horizon on the shelf since preindustrial times.

Finally, we can estimate how anthropogenic CO_2 has influenced the historical values of $p\text{CO}_2$ at the FHL dock. We assume representative values for the FHL dock of $T = 8.2^\circ\text{C}$, $S = 30.5$ and alkalinity and DIC values of $2080 \mu\text{mol L}^{-1}$ and $2000 \mu\text{mol L}^{-1}$, respectively (Fig. 2). If we subtract the

anthropogenic contribution to DIC ($36 \mu\text{mol L}^{-1}$) we calculate (from DIC and alkalinity) that the preindustrial $p\text{CO}_2$ at the FHL dock would have been about $442 \mu\text{atm}$. It's important to point out that DIC and alkalinity are capacity variables in the carbonate system, while $p\text{CO}_2$ and pH are calculated and non-linear (Stumm and Morgan 1996), so what may seem to be small changes in DIC can result in large changes in $p\text{CO}_2$. Our estimated preanthropogenic value of $p\text{CO}_2$ is about $200 \mu\text{atm}$ less than present day values but shows that some level of acidified ocean conditions probably existed around the San Juan Islands for as far back in the past as the present wind-drive upwelling system has existed (perhaps for much of the Holocene). The biological community in the San Juan Islands must be well adapted to high values of $p\text{CO}_2$ (and thus low pH) (Kelly and Hofmann 2012).

Why no blooms at the FHL dock

The conditions of HNLC at the FHL dock continued during the duration of this time series. The water adjacent to the dock at FHL exchanges rapidly with the deep San Juan Channel and other passageways (e.g., Haro Strait) between the islands, and ultimately with the Strait of Juan de Fuca. Surface nitrate concentrations are high throughout the region due to the large natural nutrient input from upwelling on the outer Washington coast (Mackas and Harrison 1997). There is a strong correlation of nitrate with salinity, especially in the > 50 m deep layer. The density structure and mixed layer depth are controlled by the salinity (e.g., Masson 2006). In the Strait of Juan de Fuca the surface mixed layer is relatively deep (> 50 m) throughout the year while the euphotic zone is relatively shallow (~ 25 m) (Mason and Pena 2009). So phytoplankton have abundant nutrients but limited light. Thus average growth conditions are poor. HNLC conditions exist at FHL and the San Juan Islands because the mixed layer depth is much greater than the euphotic zone in the waters of the surrounding straits and channels.

Division of contributions

The carbonate chemistry analytical lab was set up by Michael O'Donnell and Evan Howard and was directed by Emily Carrington. Cory Bantam and Evan Howard constructed the mesocosm facility with help from the FHL Maintenance Group led by Fred Ellis. Barbara Paul analyzed the nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), Mike Foy led implementation of the sampling, Amanda Fay, Molly Roberts and Cory Bantam did DIC and alkalinity analyses. All were involved in the sampling.

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Acknowledgments

We thank The Educational Foundation of America (EFA) and National Science Foundation Field Station Marine Lab Program (FSML) (NSF DBI

0829486) for essential initial funding to JWM to develop the Ocean Acidification Experimental Lab (OAEL). Additional support was provided by NSF award EF1041213 to E. Carrington Ken Sebens for encouragement to involve students in this research as part of a FHL mini-apprenticeship course. Students in FHL Research Apprenticeship courses, Teresa Schaut and Ashley Tonge, shared the chlorophyll and oxygen

analyses in 2012 and Natsuko Porcino did chlorophyll and Andrew Baird did oxygen in 2013. Fred Ellis and the FHL Maintenance Team for maintaining and repairing the lab facilities.

Submitted 14 January 2015

Accepted 20 January 2015